



TITLE:

Synthesis of Vinyl Ether-Based Polymacromonomers with Well-Controlled Structure (ORGANIC MATERIALS CHEMISTRY-Polymeric Materials)

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Synthesis of Vinyl Ether-Based Polymacromonomers with Well-Controlled Structure

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The present paper focuses on the atom transfer radical polymerization (ATRP) of vinyl ether (VE)-based macromonomers with a methacryloyl group at the chain end. Living cationic polymerization of isobutyl VE (IBVE) initiated with the HCl adduct of a VE carrying a pendant methacryloyl group in conjunction with ZnI_2 yielded the macromonomer (MA-PIBVE) with a narrow molecular weight distribution (MWD) ($M_w/M_n < 1.1$). The ATRP of MA-PIBVE was carried out using a halide initiator and the $\text{CuBr}/4,4'$ -di-*n*-heptyl-2,2'-bipyridine catalytic system. The number-average molecular weight of the polymacromonomer increased in proportion to the monomer conversion, while the MWDs stayed fairly narrow ($M_w/M_n \sim 1.2$). Thus polymacromonomers with controlled chain lengths for both the backbone and the side chain have been synthesized for the first time through a combination of living cationic polymerization and ATRP techniques.

Keywords: Polymacromonomer / Living cationic polymerization / Controlled radical polymerization

Recently there has been increasing interest in polymacromonomers, which are prepared by the homopolymerization of macromonomers. They are regular multi-branched macromolecules characterized by an extremely high branch density along the backbone. They can have unique molecular morphologies ranging from star-shaped spheres to rod-like cylinders, depending on the degrees of polymerization (DP) of the backbone and branch chains. For instance, polymacromonomers with a sufficiently large DP and long branches have been reported to exhibit a lyotropic phase. It was not until recently that the radical homopolymerization of a macromonomer in a highly concentrated medium yielded polymacromonomers with a high DP. Still more

difficult has been the living polymerization of macromonomers in a controlled manner.

On the other hand, the recent development in the controlled/ "living" radical polymerizations employing several initiating systems has provided possibilities for the synthesis of polymers with well-controlled structure. The transition metal-catalyzed atom transfer radical polymerization (ATRP) is one of the versatile techniques to achieve a controlled radical polymerization. Herein, we report on the ATRP of isobutyl vinyl ether (IBVE)-based macromonomers with the methacryloyl group at the initiating end (MA-PIBVE). This macromonomer is synthesized by living cationic polymerization. The combined use of living cationic polymerization and ATRP has led

ORGANIC MATERIALS CHEMISTRY — Polymeric Materials —

Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and for the development of various types of polymers with controlled structure and/or novel functions. Among those have been the studies on (1) the mechanism and kinetics of "living" radical polymerization and its applications to the synthesis of well-defined polymers and copolymers of varying architecture, (2) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, and (3) the structure of polymer gels, ultrathin films and polymer alloys.



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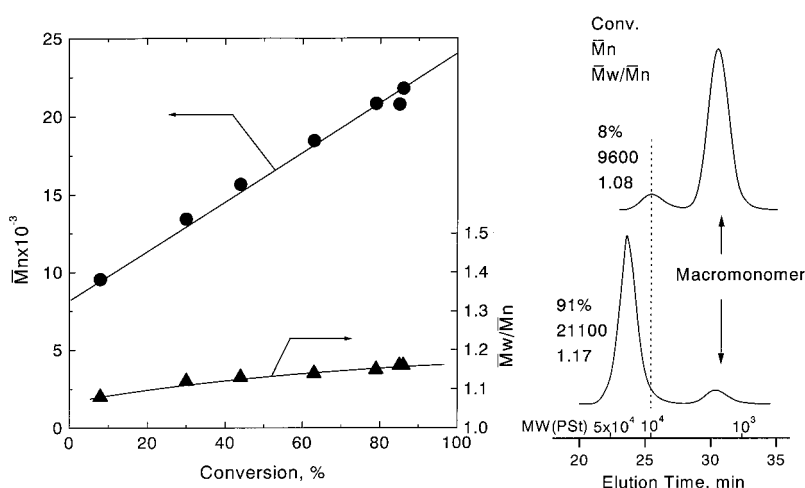
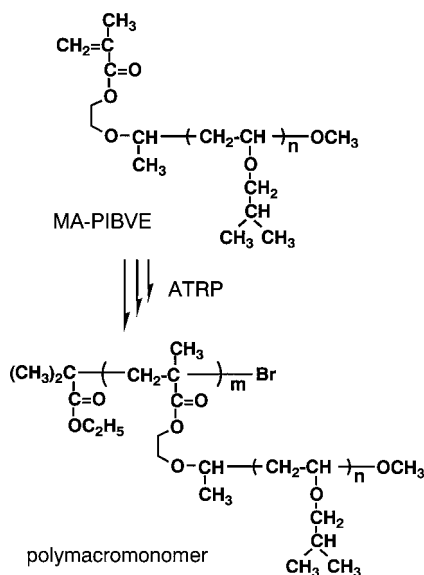


Figure 1. M_n , M_w/M_n , and MWD curves of polymacromonomers obtained by the ATRP of MA-PIBVE ($M_n = 1.6 \times 10^3$) in diphenyl ether (50 wt.-%) at 50 °C: $[M]_0/[ethyl\ 2-bromoisobutyrate]_0/[CuBr]_0/[dHBipy]_0 = 30/1/1/2$ (molar ratio).

to a new type of well-defined polymacromonomer that is controlled with respect to both backbone and side chain lengths and length distributions [1].

Synthesis of Macromonomers

The living cationic polymerization of IBVE was conducted by the HCl adduct of 2-(vinylxy)ethyl methacrylate (VEM-HCl) as the initiator in conjunction with zinc iodide (ZnI_2) to give the macromonomer (MA-PIBVE) with a narrow molecular weight distribution ($M_w/M_n < 1.1$). The number-average end functionality (F_n) estimated by the 1H NMR analysis was close to unity, indicating that the macromonomer has one methacryloyl group at the initiating end. The estimated number-average degrees of polymerization (DP_n s) of MA-PIBVE were in good agreement with the IBVE/initiator (VEM-HCl) feed molar ratios. All the obtained macromonomers have a narrow molecular weight distribution (MWD) and controlled DP_n .

ATRP of Macromonomers

The polymerization of MA-PIBVE by ATRP was conducted under a homogeneous condition using 4,4'-di-*n*-heptyl-2,2'-bipyridine (dHBipy) as the ligand, which coordinates copper(I) to solubilize the resulting complexes in the polymerization medium. The polymerization was carried out using ethyl 2-bromoisobutyrate as the initiator in conjunction with copper(I) bromide (CuBr) in diphenyl ether solution (50 wt.-%) at 50 °C [2]. The polymerization of MA-PIBVE ($M_n = 1.6 \times 10^3$) with a molar ratio $[M]_0/[I]_0/[CuBr]_0/[dHBipy]_0 = 30/1/1/2$ smoothly occurred without an induction period, and the conversion reached ca. 90% in 5 h. Moreover, the plot of $\ln[M]_0/[M]$ versus time was linear up to about 70%-conversion, indicating that the number of growing radicals remained constant. Deviations from the linear line were observed at higher conversions. This might be attributed to the increasingly high viscosity of the polymerization medium

rather than to irreversible termination reactions such as recombination of growing radicals.

As shown in Figure 1, the number-average molecular weights (M_n) of the obtained polymacromonomers increased linearly with the conversion, while the MWDs stayed fairly narrow with $M_w/M_n < 1.2$. These M_n and M_w/M_n values were estimated by polystyrene-calibrated GPC, and hence they are apparent values. Static light scattering measurements were made for one of the polymacromonomers. The weight-average molecular weight (M_w) determined by light scattering was 5.0×10^4 . This value is much larger than the GPC value ($M_w = 2.4 \times 10^4$) but reasonably well agrees with the theoretical value of 4.2×10^4 calculated from $M_w = M_{n,calcd} \times (M_w/M_n)_{GPC}$, where $M_{n,calcd}$ is the M_n value calculated with the initiator to (converted) monomer ratio, and $(M_w/M_n)_{GPC}$ is the GPC polydispersity index. All these results support the "living" nature of the ATRP of MA-PIBVE. The small value of M_w (or M_n) estimated by GPC suggests the multi-branched structure of the polymacromonomer that is more compact in hydrodynamic volume than the linear analog with a similar molecular weight.

Experiments were also carried out with higher $[M]_0/[I]_0$ ratios. Preliminary experiments using MA-PIBVE of $M_n = 1.6 \times 10^3$ with the molar ratios of $[M]_0/[I]_0/[CuBr]_0 = 60/1/1$ and $100/1/1$ showed that the polymerization proceeded too slowly or did not occur at all. We then attempted polymerization with an increased $[CuBr]_0/[I]_0$ ratio to promote polymerizability. In all cases up to the ratio of $[M]_0/[I]_0 \sim 200$, the polymerization proceeded in a controlled manner to give polymacromonomers with a narrow MWD.

References

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